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Exploring the efficacy of Pd-Au decorated ZnO nanoparticles obtained by green synthesis as sustainable approach for water treatment

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INTRODUCTION & AIM

Photocatalysts are interesting materials for elimination of pollutants in air and in water, because of their ability to create photogenerated conduction band electrons and valence band holes, which enable redox reactions with adsorbed aqueous species. ZnO, with a wide band gap of 3.2 eV, is an attractive photocatalyst owing to its low cost, high stability, and environmental friendliness. However, its activity is limited to UV or near-UV light, which represents only about 5% of solar radiation, restricting large-scale applications. To enable visible-light response, a common approach is to couple ZnO with narrow band gap semiconductors. Recently, semiconductor–metal heterostructured nanomaterials have gained attention for combining the distinct advantages of metals and semiconductors, while exhibiting enhanced photocatalytic performance through synergistic interactions between the two components.

Aims

- Synthesis, characterization and testing of ZnO and Pd-Au/ZnO based photocatalyst materials obtained by ecological methods.
- Exploring nitrate photoreduction in drinking water, comparing plain ZnO nanoparticles (ZnO NPs) with Pd-Au decorated ZnO NPs.
- The effect of formic acid as the reductant and/or hole scavenger under similar reaction conditions.

METHOD

ZnO nanoparticles were synthesized through green chemistry by using black tea solid waste extract and zinc acetate dihydrate. The plant assisted reduction of metal nanoparticles was studied. Bimetallic nanoparticles of around 10 nm were obtained in a "green" way by simply adding a solution containing the gold precursor ($HAuCl_4$) and paladium precursor $Pd(NO_3)_2$ in a tannic acid solution.

The photocatalyst Pd-Au/ZnO was obtained by dispersing the nanoparticles, previously dissolved by sonication in deionized water on ZnO. The bimetallic nanoparticles were dried at 100 °C for 2 h and then calcined at 300 °C for 1 h. The final metal loading of support oxides was 1 wt%.

The photocatalytic experiments were carried out in photoreactor system by nitrate reduction under solar simulator. The nitrate reduction was evaluated at 18 °C under simulated solar light AM 1.5 (1000W/m^2) with formic acid as the reductant and/or hole scavenger.

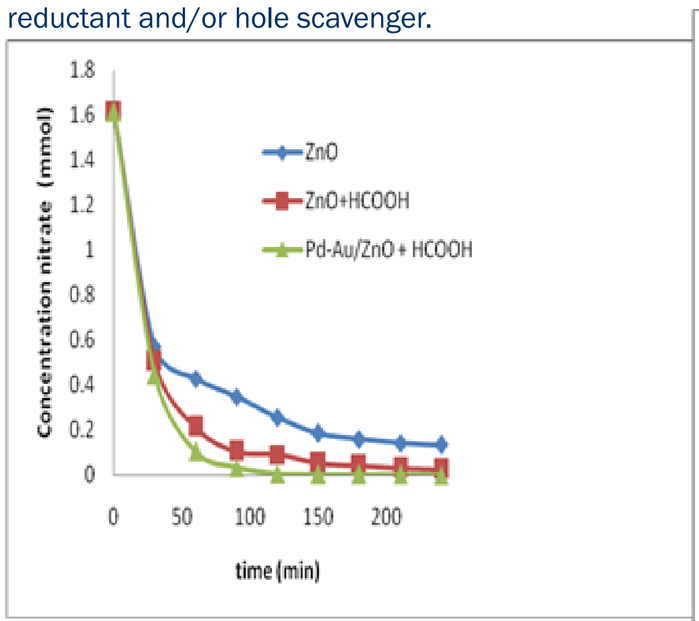


Figure 3. Time dependence of photocatalytic activity on ZnO and Pd-Au/ZnO

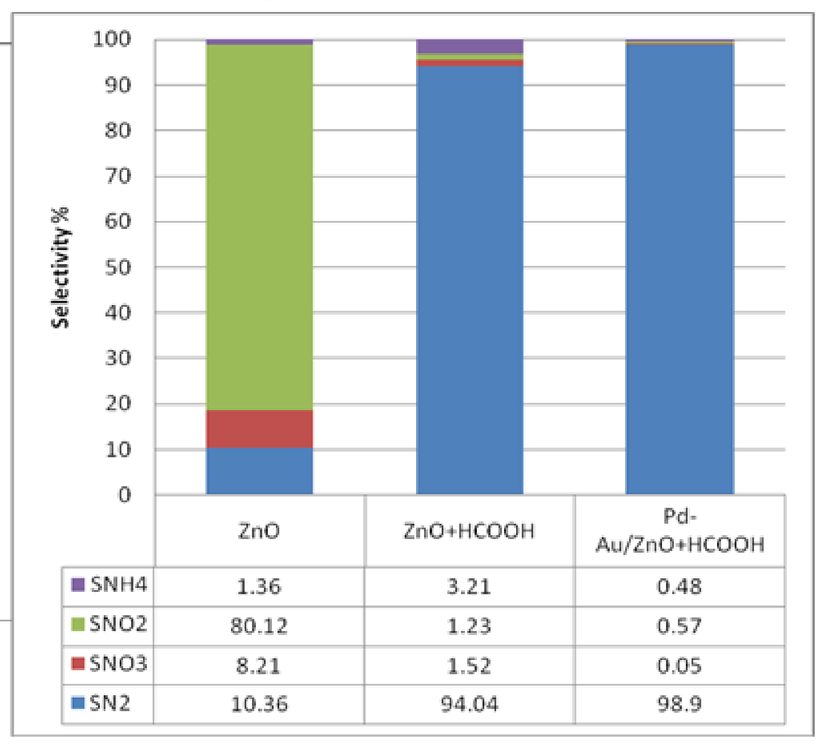


Figure 4. Selectivity to N_2, NO_2^-, NH_4^+ and NO_3^- in photocatalytic reaction of nitrate reduction on ZnO and Pd-Au/ZnO nanoparticles after four hours (240 min).

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2 \quad (1)$$

$$2\,NO_2^- + 6e^- + 8H^+ \rightarrow N_2 + 4H_2O \quad (2)$$

$$2\,NO_2^- + 6e^- + 8H^+ \rightarrow NH_4 + 2H_2O \quad (3)$$

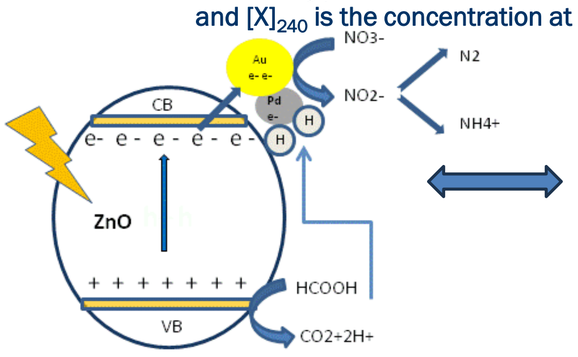
The selectivity to nitrite and ammonium were calculated as:

$$S(NO_2^-)\% = [NO_2^-]_{240}/([NO_3^-]i - [NO3^-]_{240}) * 100 \quad (4)$$

$$S(NH_4^+)\% = [NH_4^+]_{240}/([NO_3^-]i - [NO_3^-]_{240}) * 100 \quad (5)$$

$$S(NO_3^-)\% = [NO_3^-]_{240}/([NO_3^-]i - [NO3^-]_{240}) * 100 \quad (6)$$

where $[NO_3]_i$ is the concentration before irradiation and $[X]_{240}$ is the concentration at time = 240 min



Possible mechanism for nitrate reduction on Pd-Au/ZnO

RESULTS

The surface and chemical state analysis of pure ZnO and Pd-Au decorated ZnO were investigated by XRD, IR-spectroscopy, TEM, and SEM.

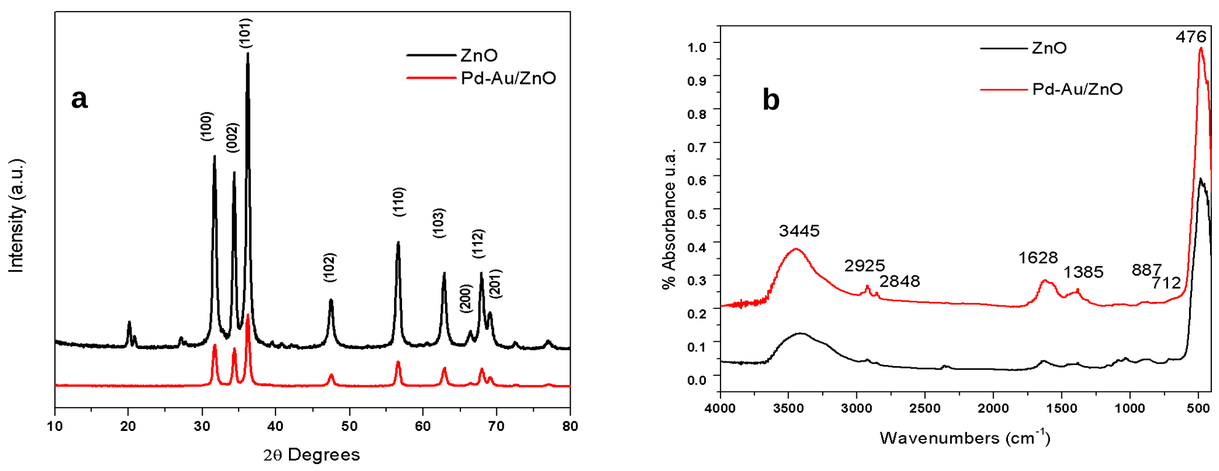


Figure 1. XRD (a) and FTIR spectra (b) of ZnO materials

The XRD diffractograms of ZnO an Pd-Au/ZnO show the presence of unique structure of ZnO and Pd-Au. The absorption peak was observed in the range of 3000-3600 cm^{-1} centered at 3445 cm^{-1} corresponding to the stretching vibration of intermolecular hydrogen bond (O-H) from FT-IR.

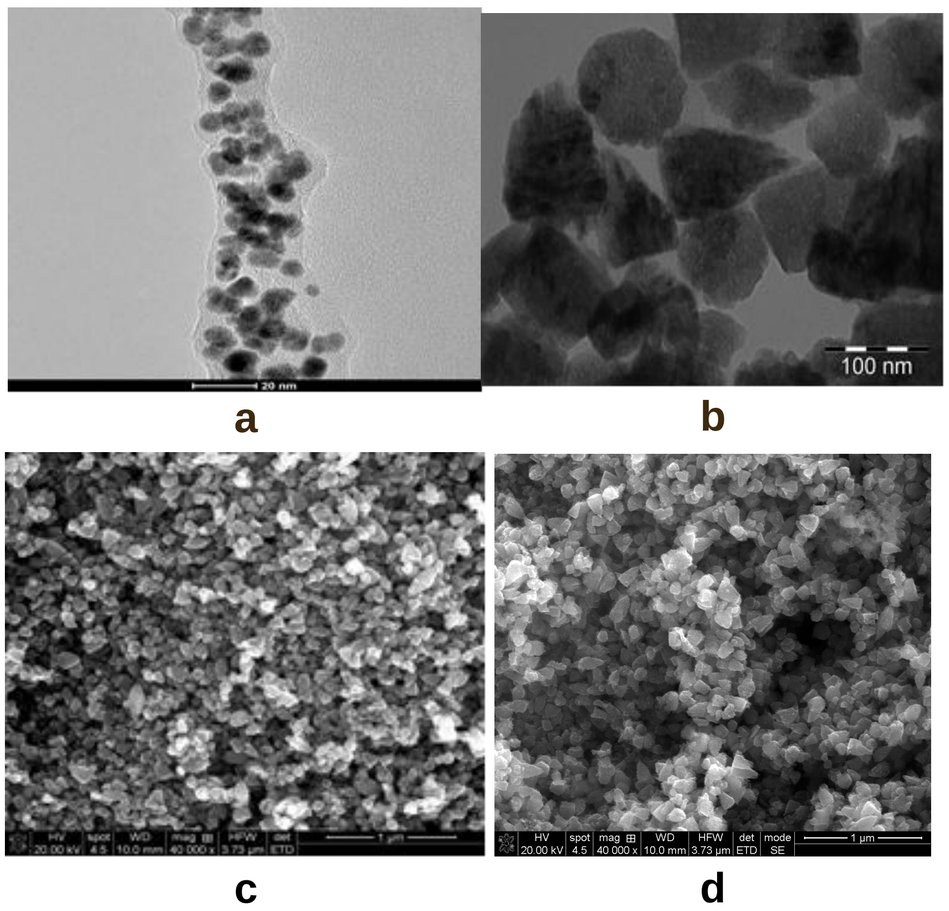


Figure 2. TEM images of Pd-Au NPs (a) and ZnO NPs (b) and SEM image for ZnO (c), and Pd-Au /ZnO (d).

CONCLUSION

The ZnO nanoparticles with sizes between 100-150 nm with the wurtzite phase were synthetized by a green synthetic route using the black tea extract.

Bimetallic Pd-Au nanoparticles of around 10 nm obtained in a "green" way employing tannic acid were deposited on zinc oxide.

The photocatalytic performance of ZnO NPs and Pd-Au/ZnO deposited towards the removal of nitrate was evaluated both in the absence and presence of the formic acid as the reductant and/or hole scavenger.

N_2 selectivity is dramatically enhanced by the presence of the formic acid as in the same experimental conditions.

Acknowledgements

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